CERIA/ZIRCONIA FIBRES FOR USE IN CIGARETTES

FIELD OF THE INVENTION

The invention relates to incorporation of ceria/zirconia fibres into an individual component of a cigarette, in particular, cigarette components such as a cigarette paper/wrapper, tobacco, and/or filter.

BACKGROUND OF THE INVENTION

Metal oxide catalysts have been incorporated onto the surface of various types of fibres for decomposing various compositions or for purifying exhaust gases. For example, U.S. Patent 5,094,222 describes a mixture of ceramic fibres containing an oxidation catalyst for decomposition of fats and oils. The ceramic fibres are made from at least one of the following oxides: silicon oxide, zirconium oxide and aluminum oxide and the oxidation catalyst is selected from at least one of a variety of metal oxides. U.S. Patent 5,165,899 describes a porous fibrous structure for purification of exhaust gases. The fibrous structure is made of metal alloy fibrils of the MCrAlX type where M is a matrix chosen from iron, and/or nickel and/or cobalt and X is chosen from zirconium, yttrium, cerium and lanthanum metal.

Several patents refer, more specifically, to various processes for making metal oxide/zirconium oxide fibres. U.S. Patent 5,468,548 describes a process for making reinforced fibres for high temperature composites consisting of a matrix and eutectic fibres dispersed in the matrix. The eutectic fibres can be selected from a series of metal oxides and the reference suggests several optional metal oxides including ceria and zirconia. U.S. Patent 3,891,595 describes the process of making friction materials that contain 40-85% of a synthetic inorganic refractory metal oxide fibre and 15-35% of a binder. The metal oxide fibre may contain zirconia and 1-10% of a stabilizer, such as alkaline oxides, yttria and rare earth oxides.

U.S. Patents 4,927,622, 5,053,214 and 5,112,781 describe a process that involves making an aqueous solution of zirconium-based granules and a phase stabilizer (1-35 wt%), such as calcium, yttrium, cerium and hafnium oxides, and fiberizing the solution. This particular process involves making and drying the zirconium-based granules before making the fibre.

U.S. Reissued Patent 35,143 describes a process for making a ceramic fibre that involves mixing crystalline zirconium grains, a zirconia compound, solvent and a phase stabilizer (more than 0 and up to 20 mol% of the stabilizer).

Although these references disclose various uses of metal oxide/zirconia fibres, none have attempted to specifically combine such fibres with known cigarette technology.

In the cigarette industry, various attempts have been made to incorporate specific fibres and other additives into cigarettes. For instance, U.S. Patent 2,755,207 describes a cigarette paper that yields a smoke substantially free of obnoxious components. The cigarette paper is made from cellulosic fibre, which has intimately associated therewith a finely divided mineral type siliceous catalyst material and functions like a catalyst in modifying the combustion of the paper.

Published International Patent Application WO 99/53778 describes a non-combustible sheet of treatment material for reducing sidestream smoke emissions. The sheet is used as a wrap and is applied over conventional cigarette paper of a conventional cigarette. The wrap has a very high porosity to allow the cigarette to burn at or close to conventional free-burn rates while at the same time reduce visible sidestream smoke emissions. The non-combustible wrap includes non-combustible ceramic fibres, non-combustible activated carbon fibres as well as other standard materials used in making the wrap. The wrap also includes zeolites or other similar sorptive materials and an oxygen donor/oxygen storage metal oxide oxidation catalyst. The non-combustible wrap provides an acceptable degree of sidestream smoke control,

however, due to the non-combustible nature of the wrap, a charred tube remains.

U.S. Patents 4,433,697 and 4,915,117 describe the incorporation of ceramic fibres in a cigarette paper manufacture. U.S. Patent 4,433,697 describes at least 1% by weight of certain ceramic fibres in the paper furnish in combination with magnesium oxide and/or magnesium hydroxide fillers to reduce visible sidestream smoke emanating from the burning cigarette. The furnish of fibre pulp, ceramic fibres and fillers are used to make a paper sheet on conventional paper making machines. The ceramic fibres are selected from the group consisting of polycrystalline alumina, aluminum-silicate and amorphous alumina. A filler of magnesium hydroxide or magnesium oxide is used and is coated on or applied to the fibres of the sheet.

U.S. Patent 4,915,117 describes a non-combustible sheet for holding tobacco. The thin sheet is formed from ceramic materials which upon burning produces no smoke. The ceramic sheet comprises a woven or non-woven fabric of ceramic fibre or a mixture of paper and ceramics thermally decomposed at high temperature. The ceramic fibre may be selected from inorganic fibres such as silica fibre, silica-alumina fibre, alumina fibre, zirconia fibre, or alumino borosilicate and glass fibre. The ceramic sheet is formed by binding these materials using inorganic binders such as silica gel or alumina gel. The fibres are preferably 1 to 10 micrometers in diameter.

Published International Patent Application WO 02/024005 describes a sidestream smoke treatment composition which is particularly adapted to reduced sidestream smoke emissions. The composition comprises an oxygen storage and donor metal oxide oxidation catalyst and an essentially non-combustible finely divided porous adjunct for the catalyst. Cerium oxide is a particularly preferred oxygen donor material. The porous adjunct is preferably zeolites but also includes zirconia, titania, ceria, alumina, zirconium fibres and milled porous ceramic fibres.

SUMMARY OF THE INVENTION

In one aspect of the present invention, there is provided a cigarette comprising a tobacco rod, a cigarette paper/wrapper for the tobacco rod, and optionally a filter, wherein at least one of the tobacco rod, the cigarette paper/wrapper and the filter comprise ceria/zirconia fibres. Preferably, the ceria/zirconia fibres contain up to about 50% by weight ceria.

In accordance with a preferred aspect of the present invention, the cigarette paper/wrapper comprises porous ceria/zirconia fibres with a surface area greater than about 20 m^2/g.

For ease of description, whenever the term cigarette is used, it is understood not only to include smokable cigarettes but any form of wrapped smokable product, such as cigars or the like. Whenever the term cigarette paper/wrapper is used, it is understood to encompass combustible and non-combustible papers and the like which may be used on cigarettes, cigars and the like. The paper/wrapper may be used as a single layer of cigarette paper or multiple layers of cigarette paper. The paper/wrapper may be applied as the sole layer of cigarette paper or as a wrap over conventional cigarette paper of a cigarette.

DETAILED DESCRIPTION OF THE INVENTION

Ceria/zirconia fibres are incorporated into an individual component of a cigarette, in particular, cigarette components such as a cigarette paper/wrapper, tobacco, and/or filter. Use of ceria/zirconia fibres in cigarettes provides an unexpected benefit of being able to incorporate a higher concentration of ceria and zirconia into the cigarette paper/wrapper without sacrificing wet strength as compared to the incorporation of ceria/zirconia particulates.

The present invention incorporates ceria/zirconia fibres, such as those described in U.S. Patents 4,927,622; 5,053,214; 5,112,781; U.S. Reissued Patent 35,143, U.S. Application Serial No. 60/318,614, entitled Zirconium/Metal Oxide Fibres, filed September 13, 2001, all of which are herein incorporated by reference, into an individual component of a cigarette,

more particularly, cigarette components such as cigarette paper/wrappers, tobacco, and filters.

Representative ceria/zirconia fibres may be made in accordance with one or more of the following processes.

The ceria/zirconia fibres may be made according to the method described in U.S. Patents 4,927,622 and its' related patents, 5,053,214 and 5,112,781. The method involves combining an aqueous solution of a zirconium compound, such as zirconium acetate, with cerium acetate (about 1 to 35 % by weight based upon the total weight of zirconia in solution). The pH of the solution is about 2 to 7. The solution is then heated at a temperature below about 180°C to evaporate the water and produce amorphous zirconium-based granules containing ceria. These granules are added to water in a weight ratio of about 4:3 and placed on drum rollers to form a viscous solution. This solution is fiberized and the resulting fibres are then sintered to yield ceria/zirconia fibres.

The ceria/zirconia fibres may also be made according to the method described in U.S. Application Serial No. 60/318,614, entitled Zirconium/Metal Oxide Fibres, filed September 13, 2001. The ceria/zirconia fibre is made by adding a solution of cerium nitrate to the polymer of Formula (I). The cerium nitrate solution is made by mixing cerium carbonate with nitric acid or by dissolving cerium nitrate in water. The solution is then admixed with a colloidal dispersion comprising the amorphous zirconium polymer of the formula:

$$[Zr_4(OH)_{12}(X)_2(H_2O)_4]_n\,(X)_{2n}.2nH_2O \qquad (I)$$

wherein X is preferably NO_3^- and n is a whole number. The mixing is done at approximately 15 to 25°C. The mixed colloidal dispersion is fiberized by conventional drawing techniques such as pulling or drawing, centrifugal spinning, nozzle injection or blow spinning. Usually a spinning aid is utilized in order for the dispersion to fibreize properly. Suitable spinning aids include

polyvinyl pyrrolidone, polyethylene oxide, polyvinylalcohol, polyurethane, polyacrylic acid salt, polyacrylamide and polyvinylmethyl ether. The ceria/zirconia fibres of this method usually have less than 15% non-fibrous material.

The ceria/zirconia fibres may be made according to the method described in U.S. Reissued Patent 35,143 (assigned to 3M). The method involves combining an aqueous solution of a zirconium compound (ie. zirconium acetate; about 20 to 80 % by weight based upon the total weight of zirconia in solution), ceria (up to about 20 % by weight based upon the total weight of zirconia in solution), an organic polymer (i.e. polyvinylpyrrolidone; about 0 to about 50 % by weight based upon the total weight of zirconia in solution) and a crystalline, colloidal zirconia sol (ie. Nyacol^{TM} Zr 100/20; about 20 to about 80 % by weight based upon the total weight of zirconia in solution). This solution was filtered and concentrated to a viscosity of about 80-90 PaSec. The viscous solution was extruded and the resulting fibres sintered to yield ceria/zirconia fibres. Depending on the use, these ceria/zirconia fibres may be continuous or discontinuous and may have a high surface area (in the range of 1 to 200 m^2/g) or low surface area (less than 1 m^2/g). It is preferred that, during the sintering step, the firing rate does not exceed 10°C /min until a temperature of about 500°C is attained. Once the fibres have been fired to 500°C, they may be very rapidly heated (i.e. 100°C /min) to higher temperatures. The fibres, when fired to less than about 1100°C, contain a high porosity and consequently a high surface area. As the fibres are fired to higher temperatures (about 1100°C to about 1400°C), their porosity and surface area decreases and the fibres possess higher tensile strengths.

Typically, the ceria/zirconia fibres used in the present invention contain up to about 50% by weight ceria and, more preferably, up to about 25% by weight. These fibres usually have a diameter greater than 5 micrometers, preferably in the range of about 8 to about 25 micrometers. The tensile strength of these fibres is, typically, about 1 to about 80 g/mm, preferably in the range of about 1 to about 50 g/mm.

It is understood that as the porosity of the ceria/zirconia fibres increases their structural strength may decrease. There are several applications for these fibres in cigarettes where the porosity of the chosen fibre compliments its' use. For example, fibres for structural and reinforcement applications would have lower porosity, whereas fibres for reducing sidestream smoke would have higher porosity. Preferably, the ceria/zirconia fibres used for reducing sidestream smoke are porous, that is, the fibres have a high surface area, particularly in the range of about 1 to about 200 m^2/g, preferably greater than about 20 m^2/g. The ceria/zirconia fibres having a surface area less than about 1 m^2/g are better suited for reinforcement applications.

The ceria/zirconia fibres may be used as follows: a cigarette paper/wrapper may be made from the ceria/zirconia fibres and wrapped over, and in substantial contact, with a conventional cigarette paper of a cigarette or a tobacco rod of a cigarette; a tube may be made from the ceria/zirconia fibres and placed on and in substantial contact with a conventional cigarette paper of a cigarette or a tobacco rod; and a cigarette paper/wrapper may comprise conventional cigarette paper/wrapper fibres (i.e. cellulosic fibres) and ceria/zirconia fibres.

The paper/wrappers described herein may be used as a single layer of cigarette paper/wrapper or multiple layers of cigarette paper/wrappers.

Reference to a normal or conventional cigarette, cigarette paper, or cigarette paper/wrapper fibres implies commercially available cigarettes, typically, having a porosity in the range of about 5 to about 50 Coresta units, sometimes as high as 110 to 120 Coresta units, and a conventional free-burn rate of about 3 to about 5 mm/min given conventional tobacco densities of about 0.20 to about 0.26 g/cc. Conventional cigarettes, at least in North America, have a circumference of about 20 to 30 mm, usually about 23 to 27 mm and a tobacco rod length of at least about 30 mm and preferably of about 55 mm, about 64 mm and about 74 mm, which has acceptable draw resistance.

When the ceria/zirconia fibre is wrapped over and in substantial contact with cigarette paper of a cigarette or the ceria/zirconia fibre tube is placed on and in substantial contact with cigarette paper of a cigarette, this arrangement permits the use of a conventional cigarette and when smoked, burns at conventional free-burn rates. The tube may be designed to reduce sidestream smoke such as described in applicant's International Application WO 98/16125. The ceria/zirconia fibre paper/wrapper works at very low porosities (refers to porosity of paper itself, not porosity of fibre) of about 0.5 through to very high porosity of about 10,000 Coresta units. Preferred porosities are usually less than 200 Coresta units and most preferred porosities are usually in the range of about 10 to 60 Coresta units. It is appreciated that the paper/wrapper incorporating ceria/zirconia fibres may also be used as a double or multiple wrap. A conventional cigarette filter may be attached to the cigarette in the usual way, typically, having a length of about 15 to about 35 mm.

The cigarettes of the present invention may be tailor made smokable cigarettes or may be made from the non-smokable type of tobacco rod, such as described in Canadian Patent 1,235,039. According to one aspect of the invention, the non-smokable type is rendered smokable when cigarette paper/wrapper made from ceria/zirconia fibres are applied thereto to form a smokable cigarette or the conventional cigarette paper is on the inside of the ceria/zirconia fibre paper/wrapper or tube and the tobacco rod is inserted therein. The tobacco rods used may contain conventional grades of tobacco, fillers, puffed tobacco and the like.

The ceria/zirconia fibre paper/wrapper may also comprise inert materials such as ceramics, clays and other suitable binders and sheet reinforcement materials.

To manufacture the cigarette paper/wrappers of the present invention, the ceria/zirconia fibre is preferably made into a sheet whereby the sheet may have a thickness normally in the range of about 0.04 mm up to about 2 mm but preferably not exceeding about 1 mm in thickness. The novel sheet

composition may be made by one or more standard continuous papermaking processes such as that described in Canadian Patent Application 2,323,126, directed to the incorporation of carbon fibres in cigarette paper manufacture, and U.S. Patent 4,915,117, directed to the incorporation of ceramic fibres in cigarette paper manufacture, the subject matter of such processes being incorporated herein by reference. The cigarette paper/wrappers, where the ceria/zirconia fibres replace conventional cigarette paper/wrapper fibres, are made by creating a fibre suspension of ceria/zirconia fibres (typically, up to 65% by weight of ceria/zirconia fibres are used in the suspension) and other conventional cigarette paper/wrapper fillers such as ceramics, clays and other suitable binders and sheet reinforcement materials. A viscosity modifier, such as an alginate, may also be added to the suspension to aid in the processing of the cigarette paper/wrapper by increasing the viscosity of the fibre suspension. To form the paper/wrapper, the fibre suspension may be spread out onto a screen or set of screens and dried to form a combustible paper/wrapper. The suspension may be further aged at an elevated temperature to evaporate any organics and develop, thereby, a porous non-combustible paper/wrapper.

As mentioned previously, the ceria/zirconia fibre can be used as a reinforcement for conventional combustible cigarette paper/wrapper fibres. This can reduce the amount of conventional combustible cigarette paper/wrapper fibres required. For instance, the fibre suspension may include cellulosic fibres and is made as suggested above. Typically, about 30 to about 40% by weight of ceria/zirconia fibres, about 30 to about 40% by weight of the combustible cigarette paper/wrapper fibres (ie. cellulosic fibres) and about 20 to about 40% by weight of the conventional cigarette paper/wrapper filler are used in the suspension.

In addition, it is known that cigarettes incorporate glass fibres into the paper/wrapper as reinforcement material, for instance, as described in U.S. Patent 4,915,117. The glass fibres may be present in the cigarette paper/wrapper up to 35% by weight and, according to the present invention, the

glass fibres are replaced with ceria/zirconia fibres using the method described above.

As taught in Applicant's International Patent Application WO 02/024005, herein incorporated by reference, various compositions are described with respect to sidestream smoke reduction. Those compositions typically include an oxygen storage and donor metal oxide oxidation catalyst and an essentially non-combustible finely divided porous adjunct for the catalyst. Preferred oxygen storage and donor metal oxide oxidation catalysts include rare earth metal oxides, particularly the lanthanide series metal oxides. Cerium oxide is a preferred oxygen donor material. These sidestream smoke reducing compositions may be applied to the surface of the cigarette paper/wrapper, may be incorporated into the cigarette wrapper/paper and/or impregnated into the cigarette wrapper/paper. When incorporating the composition into the paper/wrapper, the wet strength of the paper material during manufacture limits the amount of composition added. In accordance with the present invention, the use of ceria/zirconia fibres, and especially porous ceria/zirconia fibres, to replace a portion or all of the cellulose fibres provides for an acceptable wet strength. By virtue of the present invention, loading of ceria as an active ingredient in the sidestream smoke composition can be increased to much higher levels than that which could be attained by incorporating the sidestream smoke composition into the paper furnish. Furthermore, when higher loadings of ceria are desired, the application of coatings containing ceria is not necessary. Since the porous ceria/zirconia fibres have sidestream smoke reduction properties in some applications, the ceria/zirconia fibres may be all that is needed in the paper, whereas in other applications, a combination of porous ceria/zirconia fibres and the sidestream smoke reduction composition of our prior system may be required.

Other applications of the ceria/zirconia fibres include the incorporation of ceria/zirconia fibres into tobacco. Incorporation of the ceria/zirconia fibres may take place at any time prior to the final packaging of the tobacco product. In the case of cigarette tobacco, the fibres may be incorporated before or after

blending of the various tobaccos if, in fact, blended tobacco is employed. In addition, the fibres are dispersed throughout the treated tobacco and may be used in one or all of the blend constituents. The fibres facilitate processing of the tobacco and may enhance burn characteristics of the tobacco, such as sidestream smoke reduction. Typically, the fibres are well dispersed throughout the tobacco so that they will be uniformly effective during the entire period during which the composition is smoked.

The weight proportions of the components described above for use in tobacco are usually within the following approximate weight ranges to provide useful tobacco products. The amount of ceria/zirconia fibres added to the tobacco may be about 1 to about 15% by weight, preferably, about 1% to about 10% by weight based upon the weight of the tobacco.

The tobacco may be further processed and formed into any desired shape or used loosely (ie. cigars, cigarettes, and pipe tobacco) in a manner well-known to those skilled in the tobacco art. Other conventional tobacco additive materials, such as flavourants and humectants may be used in the practice of the present invention without deviating from the scope thereof.

Other applications of the ceria/zirconia fibres include incorporation of the ceria/zirconia fibres into a filter. In one embodiment, the ceria/zirconia fibres are placed in a cavity within the filter of the cigarette and sealed. The ceria/zirconia fibres may also be milled prior to placement within the cavity of the filter. Typically, the filter cavity length is approximately 4 mm. In another embodiment, conventional filter fibres, such as filter fibres described in Canadian Patents 1,092,933; 1,301,012; and 2,177,496, are replaced either partially or wholly with ceria/zirconia fibres. Specifically, glass fibres in cigarette filters, such as the filters described in U.S. Patent 5,829,449, are replaced with ceria/zirconia fibres.

In accordance with the present invention, at least one of the various cigarette components of the present invention comprise ceria/zirconia fibres. For instance, the ceria/zirconia fibres may be used in several different combinations within a cigarette (ie. the cigarette paper/wrapper and filter may

comprise the ceria /zirconia fibres, whereas the tobacco is conventional cigarette tobacco). All cigarette components may comprise ceria/zirconia fibres.

Although preferred embodiments of the invention have been described herein in detail, it will be understood by those skilled in the art that variations may be made thereto without departing from the spirit of the invention or the scope of the appended claims.